

Potentiostatically Controlled Olefin Metathesis

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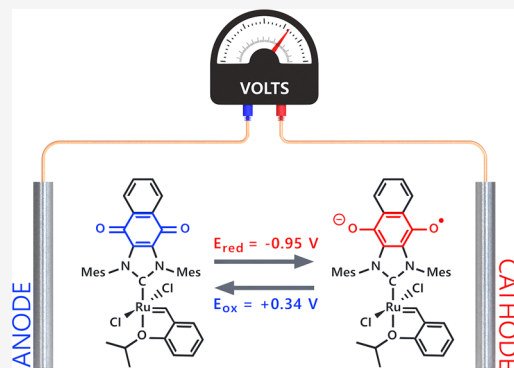


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ABSTRACT: A Ru(II) complex supported by an N-heterocyclic carbene annulated to a redox-active naphthoquinone (NQ) was interrogated using a range of potentiodynamic and potentiostatic electrochemical techniques. The complex exhibited two redox processes, one of which was attributed to the Ru(II)|Ru(III) couple ($E_{1/2} = +1.10$ V vs a saturated calomel electrode) and the other to the NQ|NQ^{•−} couple ($E_{1/2} = -0.62$ V). Using potentiostatic coulometry or bulk electrolysis, the application of a fixed negative potential (−0.95 V) to electrodes placed in a dichloromethane solution containing the complex resulted in a reduction reaction. The complex was quantitatively reduced within minutes, as determined by coulometry, and subsequently oxidized to its initial, neutral form through the application of a relatively positive potential (+0.34 V) over similar periods of time. The interconversion process was found to be reversible and used to modulate a series of ring-closing metathesis and ring-opening metathesis polymerization reactions. While relatively high activities were observed when the neutral form of the catalyst was employed, the reaction rates were attenuated upon *in situ*, potentiostatic reduction. Toggling between relatively negative or positive potentials enabled the aforementioned olefin metathesis reactions to be switched between fast and slow states.



1. INTRODUCTION

Significant efforts have been directed toward the integration of responsive units^{1–7} into contemporary catalysts in order to gain control over the corresponding catalyzed transformations.^{8–15} The units are typically designed to selectively respond to chemical (e.g., pH),^{16–19} thermal,^{20–22} photochemical,^{23–28} mechanical,^{29–31} redox,^{32–40} or electrochemical^{41–44} stimuli. The latter approaches, which include potentiostatic coulometry or bulk electrolysis (BE), feature a number of distinct advantages, including the ability to (1) finely tune the electric potential applied to the reaction mixture, (2) precisely control the extent of the reduction or oxidation reaction, and (3) modulate the redox chemistry in a temporal fashion.⁴⁵ For example, Matyjaszewski⁴⁶ demonstrated that BE can be used to modulate the kinetics of copper-catalyzed polymerizations of methyl acrylate (Scheme 1a: termed “electrochemical atom transfer radical polymerization” or eATRP). The effect was achieved by applying a relatively negative potential (−0.69 V vs Ag/Ag⁺) in order to transform copper complexes into their more active, reduced states. The subsequent application of a relatively positive potential (−0.40 V) effectively oxidized the catalysts which inhibited the polymerization reaction. Balancing the applied potential between these two states facilitated the synthesis of polymers with tunable molecular weights and narrow polydispersity. Variations of this methodology have enabled control over the polymerization of other vinyl monomers.⁴²

Electrochemical regulation of other types of catalyzed polymerizations has also been reported. For example, Fors⁴⁷ demonstrated that the chain growth of poly(vinyl ethers) can be modulated through the intermittent formation of carbocations (Scheme 1b: termed “electrochemical cationic polymerization” or eCP). Applying a relatively positive potential (e.g., +0.33 V vs Fc/Fc⁺; Fc = ferrocene) effectively oxidized a dithiocarbamate to its corresponding radical and afforded a carbocation at the terminus of a growing polymer chain.⁴⁸ Subsequent application of a relatively negative potential (e.g., −0.88 V) reduced the active species to its corresponding anion and terminated polymer growth.⁴⁹ A variety of poly(vinyl ethers) with narrow polydispersities and controlled molecular weights were obtained with this approach. Over the same time frame, Byers⁵⁰ reported an electrochemical method that enabled the chemoselective polymerization of *rac*-lactide or cyclohexene oxide (Scheme 1c: termed “electrochemical ring-opening polymerization” or eROP). Applying different potentials (e.g., +2.3 or +3.7 V vs Li⁺/Li) toggled the metal center embedded in a bis(imino)-pyridine iron alkoxide complex between two different states

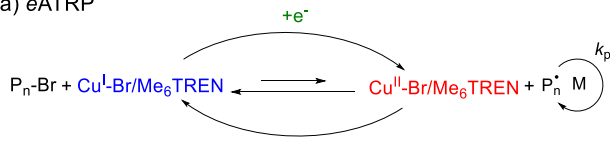
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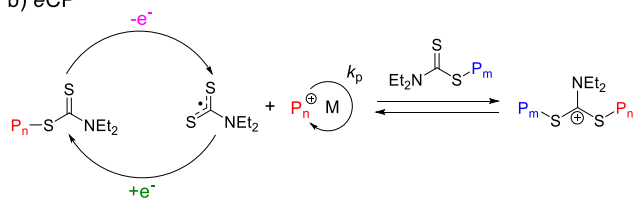


Scheme 1. Examples of Electrochemically Controlled Redox-Switchable Reactions: (a) *e*ATRP, (b) *e*CP, and (c) *e*ROP^a

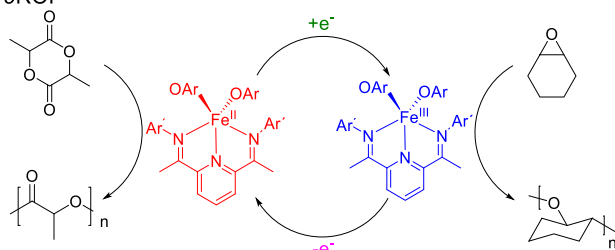
a) *e*ATRP



b) *e*CP



c) *e*ROP



^aAbbreviations: Me₆TREN = tris[2-(dimethylamino)ethyl]amine, Ar = 4-methoxyphenyl, Ar' = 2,6-dimethylphenyl.

(Fe^{II} vs Fe^{III}). The neutral form of the catalyst (Fe^{II}) polymerized *rac*-lactide, whereas the oxidized derivative (Fe^{III}) facilitated the conversion of cyclohexene oxide to its corresponding polymer.⁴⁵

We previously disclosed the Ru complex **1** (Figure 1a) and described methods for using the complex to modulate various

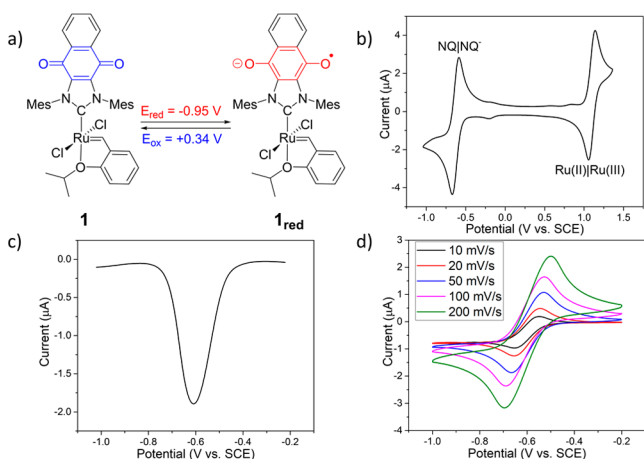


Figure 1. (a) Potentiostatic reduction and oxidation of **1**. (b) CV of **1** as recorded at 0.1 V s⁻¹. (c) DPV of **1** as recorded at 0.25 mV s⁻¹. (d) CV of **1** as recorded at different scan rates (indicated). Conditions: [**1**]₀ = 0.5 mM, [TBAPF₆] = 0.01 M, CH₂Cl₂.

olefin metathesis reactions.^{51,52} In these reports, attenuated catalytic activity was achieved by reducing the naphthoquinone (NQ) unit embedded in the catalyst; subsequent oxidation restored the catalytic activity. The redox chemistry was accomplished through the addition of stoichiometric quantities of CoCp₂ (Cp = C₅H₅⁻) or FcPF₆ to cycle **1** between its

reduced and neutral states, respectively. We reasoned that potentiostatic regulation of the oxidation state of the complex, and thus its catalytic activity, would not only circumvent the need to add stoichiometric quantities of redox agents but also promote temporal control. In a broader context, the study of the proposed transformation was envisioned to enrich our understanding of electrochemically modulating well-defined organometallic complexes using a potentiostatic methodology while establishing a new approach for controlling olefin metathesis and related types of chemical transformations.

2. RESULTS AND DISCUSSION

The electrochemical properties of **1** were first comprehensively assessed through a series of potentiodynamic experiments, including cyclic voltammetry (CV) (Figure 1b) and differential pulse voltammetry (DPV) (Figure 1c). In the former, two processes were found in the range of -1.0 to +1.5 V vs a saturated calomel electrode (SCE). One process occurred at an $E_{1/2}$ value of -0.63 V and was attributed to the NQ/NQ^{•-} couple (i.e., the interconversion of the NQ moiety and its respective semiquinone radical anion).⁵³ A second process was recorded at an $E_{1/2}$ value of +1.10 V and was assigned to the Ru(II)/Ru(III) couple.⁵⁴ Inspection of data recorded for the former revealed near-unity current and charge ratios recorded for the anodic and cathodic responses (i.e., I_{ap}/I_{cp} = 0.99 and C_{ap}/C_{cp} = 0.96, respectively). The balanced signals reflect the high reversibility of the electrochemical process associated with reducing **1**⁴⁵ and were in agreement with a DPV analysis, where a single symmetrical signal characteristic of a reversible process with a current maximum at a potential of -0.61 V was recorded.⁵⁵

To determine if the aforementioned electrochemical current responses stem from analytes that are freely diffusing and dissolved or adsorbed to an electrode,⁵⁶ a series of CV analyses were performed at different scan rates (Figure 1d). A linear relationship between the peak current (I_p) and the scan rate was observed (Figure S2), which indicated that the electron transfer process was diffusion-controlled and did not occur through surface-adsorbed species.^{45,57} On the basis of these results, **1** and its reduced derivative (**1_{red}**) appeared to remain soluble during the electrochemical transformations.⁵⁸

Next, a series of potentiostatic experiments were conducted using a three-electrode setup and a three-chamber cell (Figure S1).⁵⁹ The counter electrode was separated from the working and reference electrodes by a middle chamber to minimize the formation of byproducts.⁴⁵ The cell was loaded with a stir bar and a dichloromethane solution of **1** ([**1**]₀ = 0.5 mM) containing tetrabutylammonium hexafluorophosphate ([TBAPF₆]; 0.01 mM) as electrolyte, and a fixed potential of -0.95 V was applied. As shown in Figure 2a (red line), a diffusion-controlled current response was observed during the early stages of the electrolysis. After 10 min, the current began to decrease, which indicated that the electrolysis was becoming limited by mass transfer and reaching saturation. A color change from light green to brown, consistent with the conversion **1** → **1_{red}**,⁵¹ accompanied the change in current. After 20 min, the current approached zero, consistent with consumption of the neutral complex. Coulometry revealed that a total of 0.51 C (Figure 2b, red line) was transferred during the electrolysis experiment. The transferred charge was in good agreement with the theoretical value (0.50 C), which was based on the initial loading of the complex and a one-electron process. The slight excess of charge measured was attributed to

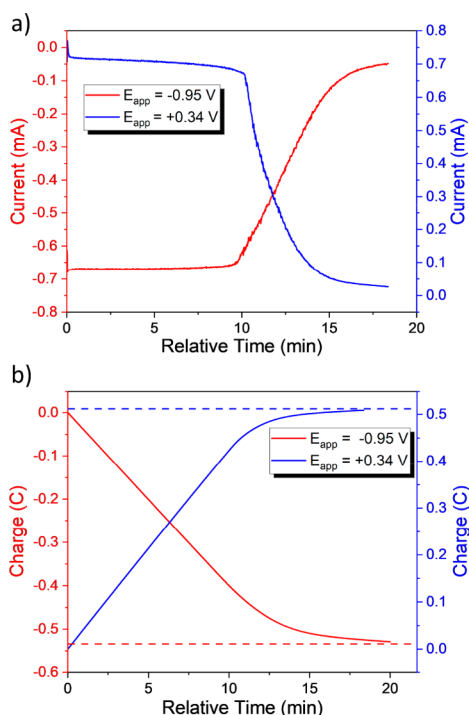


Figure 2. (a) Plots of current vs relative time upon the application of a potential of -0.95 V (red) or $+0.34$ V (blue) to a solution containing **1** or **1_{red}**. (b) Plots of charge vs relative time as obtained from the corresponding data shown in (a). Note: the data shown under oxidizing conditions (blue) were recorded after the complex was reduced (red). Conditions: $[1]_0 = 0.5$ mM, $[TBAPF_6] = 0.01$ M, CH_2Cl_2 .

non-Faradaic or capacitive processes associated with the charging of the electrical double layer at the electrode interface during electrolysis.⁴⁵ CV of the resulting solution revealed signals that were consistent with the $NQ|NQ^-$ and $Ru(II)|Ru(III)$ couples of the starting material (Figure S4a).

After the complex was reduced, a fixed potential of $+0.34$ V was applied to the aforementioned mixture. As before, the initial current response appeared to be controlled by diffusion and began to plateau over time (Figure 2a, blue line) and a reversal in color (from brown to light green) was observed. The current approached zero after 18 min, and a total of 0.52 C (Figure 2b, blue line) was transferred over the course of the experiment. Signals consistent with the $NQ|NQ^-$ and $Ru(II)|Ru(III)$ redox couples of **1** were recorded upon CV of the resulting product mixture (Figure S4b).

The aforementioned electrolysis experiments were repeated, and conversions that typically exceeded 95% were achieved within 18–20 min (Table S1). For example, over three redox cycles (Figures S5 and S6), an average of 0.52 ± 0.01 C was transferred during the reduction process, whereas 0.51 ± 0.01 C was transferred during subsequent oxidation. The number of electrons transferred during each of the aforementioned processes was confirmed to be 1 using the Faraday equation. These observations are in concordance with results that were obtained when redox reagents were used and reflect the high fidelity of the electrochemical process of **1**.^{51,52}

Inspection of the electrolysis data revealed that the diffusion-controlled reduction processes appeared to occur slightly more quickly than the subsequent oxidations. To ascertain the origin of this observation, diffusion coefficients were calculated using

the Randles–Sevcik equation. The diffusion coefficient calculated for **1** was larger than that of **1_{red}** (2.57×10^{-5} $cm^2 s^{-1}$ vs 1.47×10^{-5} $cm^2 s^{-1}$, respectively) and was attributed to the relative sizes of the corresponding species. Since the reduced complex should contain tetrabutylammonium as a counteranion and thus additional solvent molecules, it can be expected to diffuse relatively slowly in comparison to its neutral precursor.⁶⁰

Subsequent efforts were directed toward potentiostatically controlling the catalytic activity displayed by **1** in ring-closing metathesis (RCM)^{61,62} and ring-opening metathesis polymerization (ROMP)^{63–65} reactions.⁶⁶ Initial experiments were directed toward investigating the activities displayed by the neutral and the reduced forms of the complex (**1** and **1_{red}**, respectively) in the RCM of diethyl diallylmalonate (DDM). The addition of the substrate ($[DDM]_0 = 0.05$ M) to a dichloromethane solution of **1** ($[1]_0 = 0.5$ mM) containing $TBAPF_6$ (0.01 M; TBA = *n*-tetrabutylammonium) as the electrolyte and 1,3,5-trimethoxybenzene (TMB) (0.05 M) as an internal standard resulted in a reaction that proceeded with a pseudo-first-order rate constant k_1 of $8.39 \times 10^{-5} s^{-1}$ (Figure 3a), as determined by analyzing aliquots that were periodically

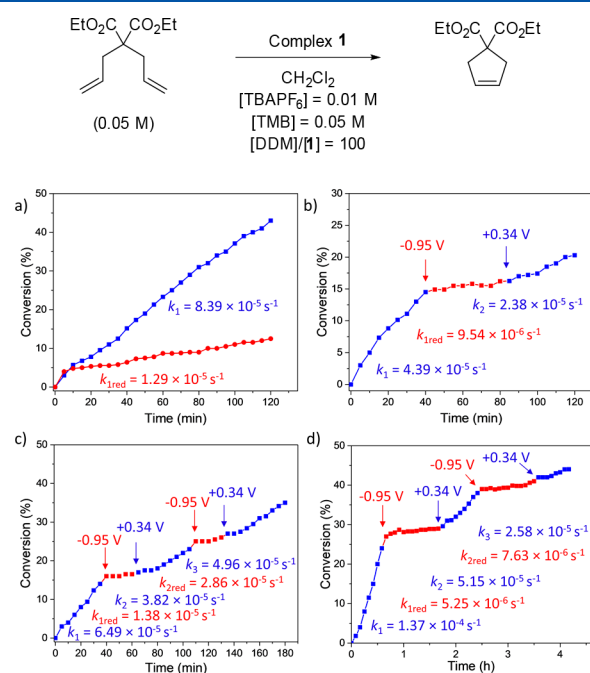


Figure 3. (a) Plots of conversion of DDM to its ring-closed product vs time as initiated with **1** (blue) or *in situ* generated **1_{red}** (red). (b) After the reaction was initiated with **1**, a potential of -0.95 V was applied (red) followed by the subsequent application of a potential of $+0.34$ V (blue). (c, d) Analogous experiments wherein the periods of applied potentials were varied. Conditions: $[DDM]_0 = 0.05$ M, $[DDM]_0/[1]_0 = 100$, $[TBAPF_6] = 0.01$ M, $[TMB] = 0.05$ M, CH_2Cl_2 .

removed from the reaction mixture over time and analyzed using gas chromatography (GC). For comparison, adding DDM to a solution of the catalyst that was first reduced using the BE method outlined above ($E_{app} = -0.95$ V, $t = 20$ min) under otherwise identical conditions resulted in a relatively slow reaction: $k_{1red} = 1.29 \times 10^{-5} s^{-1}$. The ratio of the corresponding rate constants, k_1/k_{1red} , was calculated to be 6.5; for comparison, a ratio of 6.7 was measured for analogous reactions that were performed using chemical oxidants and

reductants to effect the redox chemistry.⁵¹ The different catalytic activities that were observed can be attributed to the N-heterocyclic carbene ligand, which upon reduction stabilizes the ruthenacyclobutane resting state of the catalytic cycle in a manner that suppresses retro-[2 + 2] cycloadditions and thus decreases the rate of the RCM reaction.⁶⁷

The catalytic activity displayed by **1** after a full electrolysis cycle (reduction and oxidation) was also assessed. A cell was charged with a dichloromethane solution of **1** ($[1]_0 = 0.5$ mM) containing TBAPF₆ (0.01 M) and TMB (0.05 M). After the complex was reduced and then oxidized, DDM was added ($[DDM]_0 = 0.05$ M) and the conversion of the starting material to its ring-closed product was monitored over time by GC. The reaction proceeded with a first-order rate constant $k_1 = 8.01 \times 10^{-5} \text{ s}^{-1}$ (Figure S16), a value that agreed with the rate constant measured for the virgin catalyst under otherwise identical conditions and indicated that the initially added complex was restored after the electrolysis cycle.

Building on these results, we explored the ability to modulate the catalytic activity of **1** over the course of an ongoing reaction. As shown in Figure 3b, the RCM of DDM ($[DDM]_0 = 0.05$ M, $[DDM]_0/[1]_0 = 100$, $[TBAPF_6] = 0.01$ M, $[TMB] = 0.05$ M, CH_2Cl_2) was measured to proceed at a rate constant k_1 of $4.39 \times 10^{-5} \text{ s}^{-1}$. After 15% of the DDM converted to its ring-closed product, a potential of -0.95 V was applied to the reaction mixture and a lower rate constant was measured: $k_{1,red} = 9.54 \times 10^{-6} \text{ s}^{-1}$ ($k_1/k_{1,red} = 4.6$). When the conversion of the reaction reached 30%, a relatively positive potential (+0.34 V) was applied, which restored the catalytic activity: $k_2 = 2.38 \times 10^{-5} \text{ s}^{-1}$ ($k_2/k_{1,red} = 2.5$). Subsequent experiments were directed toward assessing the ability to alter the rate of the RCM of DDM during intermittent reduction/oxidation intervals and over various periods of time. In accord with previous results, catalytic activity was toggled between relatively fast and relatively slow states over multiple cycles by applying either a positive or negative potential, respectively. Moreover, the catalytic activity was maintained in either state for relatively short (Figure 3c) or long (Figure 3d) periods of time. While temporal control was achieved, attenuation of the activity was observed over successive redox cycles. The phenomenon was attributed to the relative instability of the alkylidene or methyldiene propagating species,⁶⁸ which may undergo premature decomposition under the reductive or oxidative conditions utilized.⁵¹

After demonstrating that BE may be used to control RCM reactions, we directed our attention toward controlling the ROMP of 1,5-cyclooctadiene (COD). Efforts began by evaluating the activities displayed by the neutral and reduced forms of the complex (**1** and **1**_{red}, respectively). Charging an electrochemical cell with COD ($[COD]_0 = 0.05$ M) and a dichloromethane solution of **1** ($[1]_0 = 0.5$ mM), TBAPF₆ (0.01 M), and TMB (0.05 M) resulted in a pseudo-first-order reaction that proceeded with a rate constant k_1 of $4.58 \times 10^{-4} \text{ s}^{-1}$ (Figure 4a), as determined by GC. In a separate experiment, the reduced form of the catalyst was first generated by applying a negative potential ($E_{app} = -0.95$ V, $t = 20$ min) to a dichloromethane solution containing **1** ($[1]_0 = 0.5$ mM), TBAPF₆ (0.01 M), and TMB (0.05 M). As observed in the RCM experiments described above, the addition of substrate (COD) to the mixture resulted in a relatively slow reaction: $k_{1,red} = 6.49 \times 10^{-5} \text{ s}^{-1}$ ($k_1/k_{1,red} = 7.1$). Similar to the aforementioned RCM reactions, the difference in catalytic

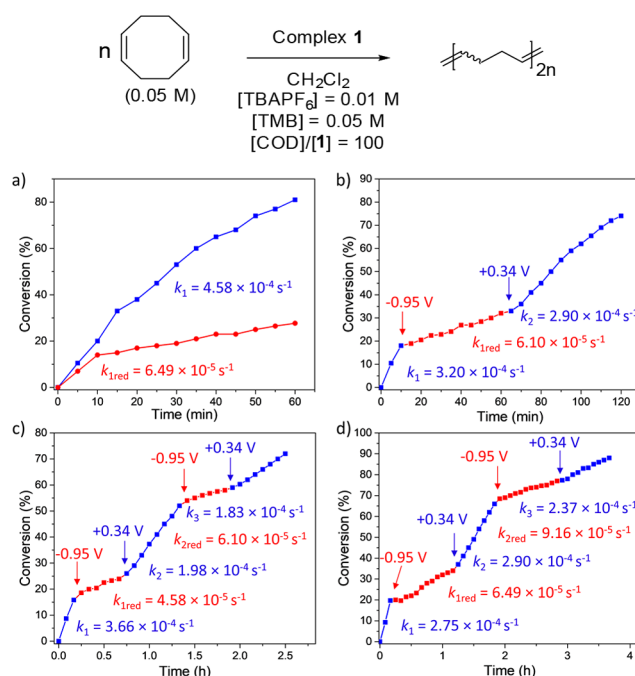


Figure 4. (a) Plots of conversion of COD to polymer vs time as initiated with **1** (blue) or *in situ* generated **1**_{red} (red), (b) After the reaction was initiated with **1**, a potential of -0.95 V was applied (red) followed by the subsequent application of a potential of $+0.34$ V (blue). (c, d) Analogous experiments wherein the periods of applied positive or negative potential were varied. Conditions: $[COD]_0 = 0.05$ M, $[COD]/[1] = 100$, $[TBAPF_6] = 0.01$ M, $[TMB] = 0.05$ M, CH_2Cl_2 .

activity was attributed to the suppression of the retro-[2 + 2] cycloaddition step of the corresponding catalytic cycle.⁶⁹

To determine if the rate constant differential may be utilized to potentiostatically control the kinetics of ROMP reactions over time, a cell was charged with a dichloromethane mixture of monomer ($[COD]_0 = 0.05$ M), electrolyte ($[TBAPF_6] = 0.01$ M), and an internal standard ($[TMB] = 0.05$ M). The addition of catalyst ($[COD]_0/[1]_0 = 100$) resulted in a ROMP reaction that proceeded with a rate constant k_1 of $3.20 \times 10^{-4} \text{ s}^{-1}$ (Figure 4b), as determined by GC. After 20% of the monomer converted to polymer, a potential of -0.95 V was applied which effectively slowed the reaction: $k_{1,red} = 6.10 \times 10^{-5} \text{ s}^{-1}$ ($k_1/k_{1,red} = 5.3$). The subsequent application of a positive potential ($+0.34$ V) restored the catalytic activity: $k_2 = 2.90 \times 10^{-4} \text{ s}^{-1}$ ($k_2/k_{1,red} = 4.8$). Moreover, the different rates were maintained for relatively short (Figure 4c) or extended periods of time (Figure 4d) and the reaction was modulated over multiple cycles by varying the applied potential.

The effect of the potentiostatically controlled kinetics on the molecular weights of the polymers obtained using the aforementioned methodology was also explored. An electrochemical cell was charged with a dichloromethane solution of monomer ($[COD]_0 = 0.05$ M), catalyst ($[1]_0 = 0.5$ mM), TBAPF₆ (0.01 M), and TMB (0.05 M). After 22% of the monomer converted to polymer, an aliquot was removed from the reaction mixture. Size exclusion chromatography (SEC) and NMR spectroscopy revealed that a polymer with a number-average molecular weight (M_n) of 13.1 kDa and a polydispersity index (\mathcal{D}) of 2.24 was produced. A potential of -0.95 V was then applied to the residual mixture. After 40 min, minimal changes in the conversion of monomer to polymer

(29%) as well as the polymer molecular weight and polydispersity ($M_n = 16.7$ kDa, $\bar{D} = 2.30$) were observed. Subsequent application of a potential of +0.34 V increased monomer conversion to 80% after 20 min and afforded a polymer with a relatively high molecular weight: $M_n = 23.4$ kDa ($\bar{D} = 2.17$). For comparison, a polymer with an M_n value of 25.6 kDa ($\bar{D} = 2.20$) was obtained when an analogous reaction was conducted in the absence of an applied potential and after reaching a similar monomer conversion (81%).

3. CONCLUSIONS

In summary, a potentiostatic approach for controlling olefin metathesis reactions was developed. The attendant methodology employs bulk electrolysis, which was used to toggle a redox-switchable catalyst between reduced and oxidized states. The process proceeded to high conversions and with high fidelity, as determined by a series of electrochemical techniques. The feature was utilized in a series of ring-closing metathesis and ring-opening metathesis polymerization reactions where catalytic activities were switched between two different states through the application of different applied potentials. Moreover, variation of the applied potentials enabled control over the olefin metathesis reactions over time. The methodology described herein not only provides a template for examining and developing potentiostatically controlled reactions that are catalyzed by organometallic complexes but also obviates the need for redox agents and enables the use of electrochemical feedback (e.g., potential, current, and total charge transferred) to inform control. Finally, this work effectively expands bulk electrolytic methods beyond radical-triggered syntheses and thus can be expected to facilitate the development of other types of redox-switchable transformations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.0c00052>.

Additional experimental details and electrochemical data, control experiments, kinetics data for the RCM and ROMP experiments, and polymer characterization data (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

BE, bulk electrolysis; CV, cyclic voltammetry; CoCp₂, cobaltocene; COD, 1,5-cyclooctadiene; DDM, diethyl diallylmalonate; Fc, ferrocene; RCM, ring-closing metathesis; ROMP, ring-opening metathesis polymerization; TMB, 1,3,5-trimethoxybenzene; SCE, saturated calomel electrode; NQ, naphthoquinone; TBAPF₆, tetrabutylammonium hexafluorophosphate.

■ REFERENCES

- (1) Luca, O. R.; Crabtree, R. H. Redox-Active Ligands in Catalysis. *Chem. Soc. Rev.* **2013**, 42 (4), 1440–1459.
- (2) Peris, E. Smart N-Heterocyclic Carbene Ligands in Catalysis. *Chem. Rev.* **2018**, 118 (19), 9988–10031.
- (3) Ryu, Y.; Ahumada, G.; Bielawski, C. W. Redox- and Light-Switchable N-Heterocyclic Carbenes: A “Soup-to-Nuts” Course on Contemporary Structure–Activity Relationships. *Chem. Commun.* **2019**, 55 (31), 4451–4466.
- (4) Choudhury, J. Recent Developments on Artificial Switchable Catalysis. *Tetrahedron Lett.* **2018**, 59 (6), 487–495.
- (5) Lyaskovskyy, V.; de Bruin, B. Redox Non-Innocent Ligands: Versatile New Tools to Control Catalytic Reactions. *ACS Catal.* **2012**, 2 (2), 270–279.
- (6) Wei, J.; Diaconescu, P. L. Redox-Switchable Ring-Opening Polymerization with Ferrocene Derivatives. *Acc. Chem. Res.* **2019**, 52 (2), 415–424.
- (7) Feringa, B. L.; Browne, W. R. In *Molecular Switches*; Feringa, B. L., Browne, W. R., Eds.; Wiley-VCH: Weinheim, Germany, 2011.
- (8) Teator, A. J.; Lastovickova, D. N.; Bielawski, C. W. Switchable Polymerization Catalysts. *Chem. Rev.* **2016**, 116 (4), 1969–1992.
- (9) Blanco, V.; Leigh, D. A.; Marcos, V. Artificial Switchable Catalysts. *Chem. Soc. Rev.* **2015**, 44 (15), 5341–5370.
- (10) Luning, U. Switchable Catalysis. *Angew. Chem., Int. Ed.* **2012**, 51 (33), 8163–8165.
- (11) Leibfarth, F. A.; Mattson, K. M.; Fors, B. P.; Collins, H. A.; Hawker, C. J. External Regulation of Controlled Polymerizations. *Angew. Chem., Int. Ed.* **2013**, 52 (1), 199–210.
- (12) Guillaume, S. M.; Kirillov, E.; Sarazin, Y.; Carpentier, J.-F. Beyond Stereoselectivity, Switchable Catalysis: Some of the Last Frontier Challenges in Ring-Opening Polymerization of Cyclic Esters. *Chem. - Eur. J.* **2015**, 21 (22), 7988–8003.

- (13) Ogawa, K.; Goetz, A.; Boydston, A. Developments in Externally Regulated Ring-Opening Metathesis Polymerization. *Synlett* **2016**, 27 (02), 203–214.
- (14) Kaiser, J. M.; Long, B. K. Recent Developments in Redox-Active Olefin Polymerization Catalysts. *Coord. Chem. Rev.* **2018**, 372, 141–152.
- (15) Teator, A. J.; Bielawski, C. W. Remote Control Grubbs Catalysts That Modulate Ring-Opening Metathesis Polymerizations. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, 55 (18), 2949–2960.
- (16) Balof, S. L.; Yu, B.; Lowe, A. B.; Ling, Y.; Zhang, Y.; Schanz, H.-J. Ru-Based Olefin Metathesis Catalysts Bearing PH-Responsive N-Heterocyclic Carbene (NHC) Ligands: Activity Control via Degree of Protonation. *Eur. J. Inorg. Chem.* **2009**, 2009 (13), 1717–1722.
- (17) Beswick, J.; Blanco, V.; De Bo, G.; Leigh, D. A.; Lewandowska, U.; Lewandowski, B.; Mishihiro, K. Selecting Reactions and Reactants Using a Switchable Rotaxane Organocatalyst with Two Different Active Sites. *Chem. Sci.* **2015**, 6 (1), 140–143.
- (18) Yoon, H. J.; Kuwabara, J.; Kim, J.-H.; Mirkin, C. A. Allosteric Supramolecular Triple-Layer Catalysts. *Science* **2010**, 330 (6000), 66–69.
- (19) Semwal, S.; Choudhury, J. Switch in Catalyst State: Single Bifunctional Bi-State Catalyst for Two Different Reactions. *Angew. Chem., Int. Ed.* **2017**, 56 (20), 5556–5560.
- (20) Coulembier, O.; Dove, A. P.; Pratt, R. C.; Sentman, A. C.; Culkun, D. A.; Mespouille, L.; Dubois, P.; Waymouth, R. M.; Hedrick, J. L. Latent, Thermally Activated Organic Catalysts for the On-Demand Living Polymerization of Lactide. *Angew. Chem., Int. Ed.* **2005**, 44 (31), 4964–4968.
- (21) Han, Y.; Zhang, S.; He, J.; Zhang, Y. Switchable C–H Silylation of Indoles Catalyzed by a Thermally Induced Frustrated Lewis Pair. *ACS Catal.* **2018**, 8 (9), 8765–8773.
- (22) Chen, C.; Bai, Z.; Cui, Y.; Cong, Y.; Pan, X.; Wu, J. Ppm-Level Thermally Switchable Yttrium Phenoxide Catalysts for Moisture-Insensitive and Controllably Immortal Polymerization of Rac-Lactide. *Macromolecules* **2018**, 51 (17), 6800–6809.
- (23) Teator, A. J.; Tian, Y.; Chen, M.; Lee, J. K.; Bielawski, C. W. An Isolable, Photoswitchable N-Heterocyclic Carbene: On-Demand Reversible Ammonia Activation. *Angew. Chem., Int. Ed.* **2015**, 54 (39), 11559–11563.
- (24) Neilson, B. M.; Bielawski, C. W. Photoswitchable Metal-Mediated Catalysis: Remotely Tuned Alkene and Alkyne Hydroborations. *Organometallics* **2013**, 32 (10), 3121–3128.
- (25) Li, M.; Zhang, P.; Chen, C. Light-Controlled Switchable Ring Opening Polymerization. *Macromolecules* **2019**, 52 (15), 5646–5651.
- (26) Neilson, B. M.; Bielawski, C. W. Photoswitchable Organocatalysis: Using Light To Modulate the Catalytic Activities of N-Heterocyclic Carbenes. *J. Am. Chem. Soc.* **2012**, 134 (30), 12693–12699.
- (27) Ogawa, K. A.; Goetz, A. E.; Boydston, A. J. Metal-Free Ring-Opening Metathesis Polymerization. *J. Am. Chem. Soc.* **2015**, 137 (4), 1400–1403.
- (28) Kaiser, J. M.; Anderson, W. C.; Long, B. K. Photochemical Regulation of a Redox-Active Olefin Polymerization Catalyst: Controlling Polyethylene Microstructure with Visible Light. *Polym. Chem.* **2018**, 9 (13), 1567–1570.
- (29) Piermattei, A.; Karthikeyan, S.; Sijbesma, R. P. Activating Catalysts with Mechanical Force. *Nat. Chem.* **2009**, 1 (2), 133–137.
- (30) Groote, R.; Jakobs, R. T. M.; Sijbesma, R. P. Mechanocatalysis: Forcing Latent Catalysts into Action. *Polym. Chem.* **2013**, 4 (18), 4846–4859.
- (31) Karthikeyan, S.; Potisek, S. L.; Piermattei, A.; Sijbesma, R. P. Highly Efficient Mechanochemical Scission of Silver-Carbene Coordination Polymers. *J. Am. Chem. Soc.* **2008**, 130 (45), 14968–14969.
- (32) Tennyson, A. G.; Lynch, V. M.; Bielawski, C. W. Arrested Catalysis: Controlling Kumada Coupling Activity via a Redox-Active N-Heterocyclic Carbene. *J. Am. Chem. Soc.* **2010**, 132 (27), 9420–9429.
- (33) Biernesser, A. B.; Li, B.; Byers, J. A. Redox-Controlled Polymerization of Lactide Catalyzed by Bis(Imino)Pyridine Iron Bis(Alkoxide) Complexes. *J. Am. Chem. Soc.* **2013**, 135 (44), 16553–16560.
- (34) Biernesser, A. B.; Delle Chiaie, K. R.; Curley, J. B.; Byers, J. A. Block Copolymerization of Lactide and an Epoxide Facilitated by a Redox Switchable Iron-Based Catalyst. *Angew. Chem., Int. Ed.* **2016**, 55 (17), 5251–5254.
- (35) Thompson, B. L.; Simons, C. R.; Heiden, Z. M. Redox Switchable Catalysis Utilizing a Fluorescent Dye. *Chem. Commun.* **2019**, 55 (76), 11430–11433.
- (36) Arumugam, K.; Varnado, C. D.; Sproules, S.; Lynch, V. M.; Bielawski, C. W. Redox-Switchable Ring-Closing Metathesis: Catalyst Design, Synthesis, and Study. *Chem. - Eur. J.* **2013**, 19 (33), 10866–10875.
- (37) Zou, W.; Pang, W.; Chen, C. Redox Control in Palladium Catalyzed Norbornene and Alkyne Polymerization. *Inorg. Chem. Front.* **2017**, 4 (5), 795–800.
- (38) Dadashi-Silab, S.; Lorandi, F.; Fantin, M.; Matyjaszewski, K. Redox-Switchable Atom Transfer Radical Polymerization. *Chem. Commun.* **2019**, 55 (5), 612–615.
- (39) Ibáñez, S.; Poyatos, M.; Peris, E. A Ferrocenyl-Benzo-Fused Imidazolyliene Complex of Ruthenium as Redox-Switchable Catalyst for the Transfer Hydrogenation of Ketones and Imines. *ChemCatChem* **2016**, 8 (24), 3790–3795.
- (40) Anderson, W. C.; Rhinehart, J. L.; Tennyson, A. G.; Long, B. K. Redox-Active Ligands: An Advanced Tool To Modulate Polyethylene Microstructure. *J. Am. Chem. Soc.* **2016**, 138 (3), 774–777.
- (41) Chmielarz, P.; Fantin, M.; Park, S.; Isse, A. A.; Gennaro, A.; Magenau, A. J. D.; Sobkowiak, A.; Matyjaszewski, K. Electrochemically Mediated Atom Transfer Radical Polymerization (eATRP). *Prog. Polym. Sci.* **2017**, 69, 47–78.
- (42) Wang, Y.; Fantin, M.; Park, S.; Gottlieb, E.; Fu, L.; Matyjaszewski, K. Electrochemically Mediated Reversible Addition-Fragmentation Chain-Transfer Polymerization. *Macromolecules* **2017**, 50 (20), 7872–7879.
- (43) De Bon, F.; Fantin, M.; Isse, A. A.; Gennaro, A. Electrochemically Mediated ATRP in Ionic Liquids: Controlled Polymerization of Methyl Acrylate in [BMIm][OTf]. *Polym. Chem.* **2018**, 9 (5), 646–655.
- (44) Trevisanella, E.; De Bon, F.; Daniel, G.; Lorandi, F.; Durante, C.; Isse, A. A.; Gennaro, A. Electrochemically Mediated Atom Transfer Radical Polymerization of Acrylonitrile and Poly-(Acrylonitrile-*b*-Butyl Acrylate) Copolymer as a Precursor for N-Doped Mesoporous Carbons. *Electrochim. Acta* **2018**, 285, 344–354.
- (45) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; Wiley: Hoboken, NJ, 2001.
- (46) Magenau, A. J. D.; Strandwitz, N. C.; Gennaro, A.; Matyjaszewski, K. Electrochemically Mediated Atom Transfer Radical Polymerization. *Science* **2011**, 332 (6025), 81–84.
- (47) Peterson, B. M.; Lin, S.; Fors, B. P. Electrochemically Controlled Cationic Polymerization of Vinyl Ethers. *J. Am. Chem. Soc.* **2018**, 140 (6), 2076–2079.
- (48) Michaudel, Q.; Chauviré, T.; Kottisch, V.; Supej, M. J.; Stawiasz, K. J.; Shen, L.; Zipfel, W. R.; Abruña, H. D.; Freed, J. H.; Fors, B. P. Mechanistic Insight into the Photocontrolled Cationic Polymerization of Vinyl Ethers. *J. Am. Chem. Soc.* **2017**, 139 (43), 15530–15538.
- (49) Nichols, P. J.; Grant, M. W. Reduction Potentials of Thiuram Disulfide/Dithiocarbamate Couples in Acetone/Water. *Aust. J. Chem.* **1982**, 35 (12), 2455–2463.
- (50) Qi, M.; Dong, Q.; Wang, D.; Byers, J. A. Electrochemically Switchable Ring-Opening Polymerization of Lactide and Cyclohexene Oxide. *J. Am. Chem. Soc.* **2018**, 140 (17), 5686–5690.
- (51) Lastovickova, D. N.; Teator, A. J.; Shao, H.; Liu, P.; Bielawski, C. W. A Redox-Switchable Ring-Closing Metathesis Catalyst. *Inorg. Chem. Front.* **2017**, 4 (9), 1525–1532.
- (52) Ryu, Y.; Shao, H.; Ahumada, G.; Liu, P.; Bielawski, C. W. Redox-Switchable Olefin Cross Metathesis (CM) Reactions and

Acyclic Diene Metathesis (ADMET) Polymerizations. *Mater. Chem. Front.* **2019**, 3 (10), 2083–2089.

(53) The signal observed at -0.2 V was unidentified and attributed to a minor decomposition or side reaction.

(54) Paradiso, V.; Bertolasi, V.; Costabile, C.; Caruso, T.; Dąbrowski, M.; Grela, K.; Grisi, F. Expanding the Family of Hoveyda–Grubbs Catalysts Containing Unsymmetrical NHC Ligands. *Organometallics* **2017**, 36 (19), 3692–3708.

(55) Stojek, Z. Pulse Voltammetry. In *Electroanalytical Methods*; Springer Berlin Heidelberg: Berlin, Heidelberg, 2010; pp 107–119.

(56) Elgrishi, N.; Rountree, K. J.; McCarthy, B. D.; Rountree, E. S.; Eisenhart, T. T.; Dempsey, J. L. A Practical Beginner's Guide to Cyclic Voltammetry. *J. Chem. Educ.* **2018**, 95 (2), 197–206.

(57) Kissinger, P. T.; Heineman, W. R. Cyclic Voltammetry. *J. Chem. Educ.* **1983**, 60 (9), 702.

(58) Likewise, Tyndall scattering was not observed upon irradiation of solutions that were subjected to the reducing conditions, indicating that the complex remained soluble in its neutral and reduced forms.^{S1}

(59) Since subquantitative reductions were observed when an H-type (two-compartment) cell was used, subsequent experiments employed the three-compartment cell described herein.

(60) Valencia, D. P.; González, F. J. Understanding the Linear Correlation between Diffusion Coefficient and Molecular Weight. A Model to Estimate Diffusion Coefficients in Acetonitrile Solutions. *Electrochem. Commun.* **2011**, 13 (2), 129–132.

(61) Monfette, S.; Fogg, D. E. Equilibrium Ring-Closing Metathesis. *Chem. Rev.* **2009**, 109 (8), 3783–3816.

(62) Ogbay, O. M.; Warner, N. C.; O'Leary, D. J.; Grubbs, R. H. Recent Advances in Ruthenium-Based Olefin Metathesis. *Chem. Soc. Rev.* **2018**, 47 (12), 4510–4544.

(63) Leitgeb, A.; Wappel, J.; Slugovc, C. The ROMP Toolbox Upgraded. *Polymer* **2010**, 51 (14), 2927–2946.

(64) Slugovc, C. The Ring Opening Metathesis Polymerisation Toolbox. *Macromol. Rapid Commun.* **2004**, 25 (14), 1283–1297.

(65) Bielawski, C. W.; Grubbs, R. H. Living Ring-Opening Metathesis Polymerization. *Prog. Polym. Sci.* **2007**, 32 (1), 1–29.

(66) A series of control experiments revealed that the conversion of DDM to its ring-closed product and the polymerization of COD were not significant in the absence of catalyst, even under applied potentials (Figures S7–S12).

(67) Rosen, E. L.; Varnado, C. D.; Tennyson, A. G.; Khramov, D. M.; Kamplain, J. W.; Sung, D. H.; Cresswell, P. T.; Lynch, V. M.; Bielawski, C. W. Redox-Active N-Heterocyclic Carbenes: Design, Synthesis, and Evaluation of Their Electronic Properties. *Organometallics* **2009**, 28 (23), 6695–6706.

(68) Hong, S. H.; Wenzel, A. G.; Salguero, T. T.; Day, M. W.; Grubbs, R. H. Decomposition of Ruthenium Olefin Metathesis Catalysts. *J. Am. Chem. Soc.* **2007**, 129 (25), 7961–7968.

(69) Lastovickova, D. N.; Shao, H.; Lu, G.; Liu, P.; Bielawski, C. W. A Ring-Opening Metathesis Polymerization Catalyst That Exhibits Redox-Switchable Monomer Selectivities. *Chem. - Eur. J.* **2017**, 23 (25), 5994–6000.